(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 628 424 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
04.11.1998 Bulletin 1998/45

(51) Int. Cl.^{6}: **B41M 5/30**, G03C 1/52

(21) Application number: **94201409.3**

(22) Date of filing: **18.05.1994**

(54) Method for marking a surface of an object by means of a laser

Laserbeschriftungsverfahren für die Oberfläche einer Gegenstands

Méthode pour marquage d'une surface d'un objet par laser

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: **26.05.1993 EP 93201505**

(43) Date of publication of application:
14.12.1994 Bulletin 1994/50

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Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

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Description

The invention relates to a method of marking a surface of an object by means of a laser light beam, according to the preamble of claim 1.

The method in accordance with the invention can be used for marking objects which are at least locally provided with a light-sensitive layer which consists of the above-mentioned mixture. The term "marking" is to be understood to mean herein: the provision of characters such as letters, numbers, symbols, figures, decorations and the like. The objects may be made of, for example metal, glass or synthetic resin. Examples of synthetic resin objects are: housings for domestic appliances and products for personal care such as shavers. Such housings are marked, *inter alia*, with a type code and are often provided with logos and coloured decorations in the form of lines and areas.

Such a method is known from United States Patent document US-A-4,742,042. In the known method a layer of a mixture consisting of a dye precursor, bis(3-allyl-4-hydroxyphenyl)sulphone as the developer, a heat-sensitive substance (heat sensitizer) and a binder are provided on a support. By locally heating said layer with, for example, a laser a coloured image is formed in said layer.

A disadvantage of the known method is that only the compounds which react with said hydroxyphenyl coupler can be used as dye precursors. According to said Patent document, fluoranes and fluorenes are suitable precursors. The colour of the dyes formed ranges from blue to green. To obtain a mixed colour a second leuco dye must be added to the mixture. In said United States Patent document no description is given of how other colours, such as violet, yellow and orange must be made. A further disadvantage is that said dyes can only be formed in a thermal process, *i.e.* using infrared radiation, and not in a photochemical process using ultraviolet radiation. A still further disadvantage is that the layer in which the dye is formed must be provided with a protective coating comprising UV-absorbing substances to improve the resistance of the colour image formed against light and other environmental factors.

It is an object of the invention to provide, *inter alia*, an alternative method which enables the entire visible colour spectrum to be provided as a marking on a surface by means of a laser and without using a second dye. In this method the dye can be formed both by thermal and photochemical processes, and a protective layer to improve the stability of the colour image can be omitted.

According to the invention, this object is achieved by a method as described in the opening paragraph, which is characterized by the characterizing part of claim 1. Azo-dyes can be repres nted by the formula A'-N=N-A" or A' =N-N=A", where A' and A" represent aromatic ring systems. Azo-dyes are in widespread use and can be obtained in any desired colour by varying the ring systems. Said dyes are often prepared by coupling a diazonium salt $A'\text{-}N^+ \equiv N$ as the precursor with a so-called coupler A"-H, *i.e.* compounds comprising active hydrogen atoms, such as indoles, phenols or anilines. Another method is the oxidative coupling of said couplers with heterocyclic hydrazones $A{>}C{=}N\text{-}NR_1R_2$, where A is a heterocyclic ring system and R_1 and R_2 represent a separable group, such as a hydrogen atom. In this method, hydrazone is activated by oxidation. For example, a Fe(III)-salt is used as the oxidation agent.

In accordance with the invention, said azo-dyes can be formed *in situ* in a thermal process by exposure to IR light if a heterocyclic hydrazone compound comprising two sulphonyl substituents R_1 and R_2, for example a bis-arylsulphonylhydrazone, a bis-alkylsulphonylhydrazone or an aryl, alkylsulphonylhydrazone, is used as the precursor. Suitable aryl groups are, for example, phenyl, tolyl, naphthyl and anthryl. Suitable alkyl groups are for example C_1-C_{10} alkyl groups which may or may not be cyclic. Suitable aromatic sulphonyl substituents are, for example, the phenylsulphonyl group and the tosyl group ($-SO_2.C_6H_5$ and $-SO_2.C_6H_4.CH_3$, respectively). Suitable alkylsulphonyl substituents are, for example, the heptylsulphonyl group and the octylsulphonyl group. Due to the presence of these long alkyl groups, the solubility of the precursor in the binders hereinafter specified is enhanced. This is an important factor in the formation of transparent layers. For the coupling reaction with, for example, an aniline, a phenol or indole no oxidation agent is necessary. Coupling takes place at a temperature above 150° C. This temperature can be attained with a CO_2 laser (wavelength 10.6 μm) having a power of 1-10 W/cm^2.

For the heterocyclic ring system A of the bis-sulphonylhydrazone use can be made of, for example, the ring systems of 3-alkylbenzothiazole (see formula I of Figure 1), such as 3-methylbenzothiazole, 4,5-tetramethylene-3-alkylthiazole (formula II), 2,4-dialkylthiadiazole (formula III), 6-alkoxy-3-alkylbenzothiazole (formula IV), 3-alkylthiazoline (formula V), 1,3-dialkylbenzimidazole (formula VI) or 3-alkylthiazole (formula VII). In said formulas, R represents an alkyl group, for example a methyl group. Other suitable heterocyclic ring systems are N-alkylquinoline, N-alkylpyridine and trialkylindoline. In said ring systems the alkyl groups may be the same or different. Bis-arylsulphonylhydrazones which can suitably be used as the precursor in accordance with the invention are, for example, bis-tosylhydrazone of 3-methylbenzothiazole (see Figure 3A) and bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole (see Figure 3B).

For the coupler use is made of compounds comprising an active hydrogen atom, such as indoles, for example, 2-alkylindole and 2-arylindole (see formula X of Figure 2, wherein R_3 is an alkyl group or aryl group, for example a methyl group or phenyl group, and R_4 is a H-atom or an alkyl group or aryl group), anilines (formula XII, wherein R_7 and R_8 are a H-atom or an alkyl

group, for example a methyl group), active methylene compounds, such as malonitrile (formula XIII) and pyrazolines (formula XI, wherein R_5 and R_6 are an alkyl group or aryl group, for example, a methyl group or phenyl group) and phenols, such as phenol, 2-naphtol and naphtol-AS (formula XIV). For the coupler use is preferably made of indoles (X) because of the higher resistance to light of the dyes formed when they are used in combination with the hereinafter specified binders.

All colours of the visible spectrum (violet, blue, green, yellow, orange, red) can be obtained by varying the heterocyclic ring system A and the coupler.

The mixture of the precursor, the coupler and a binder is provided in the form of a layer on the surface to be marked of the object. This coating process can be carried out by spraying or spin coating said mixture in a solvent. Suitable binders are 1-component lacquers and 2-component lacquers, such as epoxies, polyurethanes and polymethylmethacrylate, respectively. A suitable solvent is, for example, cyclohexanone. The mixture may contain white pigments, such as TiO_2, ZnO or SiO_2, or coloured pigments, so that a mixed colour on a coloured background is obtained.

Dependent upon the coupler used, an acid or a base is optionally added to the mixture. By virtue thereof, the coupling reaction, in which an azo-dye is formed, takes place more efficiently, so that the colour strength is improved. When a coupler in accordance with formula X or XII is used, an acid may be added; when a coupler in accordance with formula XI, XIII or XIV is used, a base may be added.
Suitable acids are, for example, benzoic acids, such as p-nitrobenzoic acid. An example of a suitable base is diazabicyclo-octane. Said substances dissolve readily in the above-mentioned binders.

The coupling reaction leading to the formation of an azo-dye based on a bis-sulphonylhydrazone can also be carried out by means of UV-light radiation, for example light originating from an excimer laser. In this embodiment, the azo-dye is formed in a photochemical process. In this case, the layer comprises a sensitizer, such as benzophenone, 4,4'-dichlorobenzophenone and 4,4'-difluorobenzophenone. If use is made of UV-light, the omission of said sensitizer causes a reduced conversion to said azo-dye.

Another embodiment of the method in accordance with the invention is characterized in that UV-laser light and a heterocyclic mono-sulphonylhydrazone are used. In this case, R_1 in the above-mentioned formula $A{>}C{=}N{-}NR_1R_2$ of the heterocyclic hydrazone represents an aromatic or alkylsulphonyl substituent and R_2 represents a H-atom. For the arylsulphonyl substituent or alkylsulphonyl substituent R_1 use can be made of the above-mentioned groups. In this embodiment, the layer also comprises a compound which acts as a sensitizer as a result of exposure to UV-light, said compound being, for example benzophenone, 4,4'-dichlorobenzophenone and 4,4'-difluorobenzophenone, and the azo-dye is formed in a photochemical process.

For the heterocyclic ring system A of the mono-sulphonylhydrazone use can be made of the above-mentioned ring systems of Figure 1. Mono-arylsulphonylhydrazones which can suitably be used as th precursor in accordance with the invention are, for example, mono-tosylhydrazone of 3-methylbenzothiazole (see Figure 4A) and mono-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole (see Figure 3B; 4,5-tetramethylene-3-methylthiazolone-(2)-[ω-p-toluenesulphonylhydrazone]).

If the heterocyclic mono-sulphonylhydrazones are used as the precursor, the above-mentioned couplers and binders can be used.

The method in accordance with the invention can very suitably be used for decorating synthetic resin products. By exposure to laser light, either UV-light or IR-light, the desired decorations or other markings can be provided in the layer. The azo-dyes formed are very resistant to environmental influences such as light and moisture, so that a protective layer can be omitted.

GB-B-974,345, US-A-3,149,990 and US-A-3,146,348 disclose heat-sensitive thermographic copy sheets wherein a composite condensation product of an azo coupler and e.g. a heterocyclic sulphonylhydrazone, and an oxidizing agent is converted to an azo-dye by a heat treatment.

The invention will be explained in greater detail by means of exemplary embodiments and drawings, in which

Figure 1 shows several structural formulas of heterocyclic ring systems of a hydrazone which can suitably be used as a precursor for the formation of azo-dyes,
Figure 2 shows several structural formulas of couplers for the formation of azo-dyes with a hydrazone,
Figure 3A shows the structural formula of bis-tosylhydrazone of 3-methylbenzothiazole,
Figure 3B shows the structural formula of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole,
Figure 4A shows the structural formula of mono-tosylhydrazone of 3-methylbenzothiazole,
Figure 4B shows the structural formula of mono-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole,
Figure 5 shows the equation of the reaction of mono-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole and 2-phenylindole, resulting in the formation of a violet azo-dye (XX),
Figure 6 shows the equation of the reaction of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole and 2-phenylindole, resulting in the formation of a violet azo-dye (XX),
Figure 7 shows the equation of the reaction of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole and 3-methyl-1-phenyl-2-pyrazoline-5-one,

resulting in the formation of an orange azo-dye (XXX),

Figure 8 shows the equation of the reaction of bis-tosylhydrazone of 3-methylbenzothiazole and 2-ph nylindole, resulting in the formation of a red azo-dye (XL),

Figure 9 shows the equation of the reaction of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole and malonitrile, resulting in the formation of a yellow azo-dye (L), and

Figure 10 shows the equation of the reaction of tosyl-octyl hydrazone of 4,5-tetramethylene-3-methylthiazole (LX) and 2-phenylindole, resulting in the formation of a violet azo-dye (XX).

<u>Exemplary embodiment 1</u>

<u>A. Preparation of mono-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole (structural formula: Figure 4B)</u>

A quantity of 20 g of 4-methylthiosemicarbazide and 36.5 g of p-toluenesulphonylchloride are dissolved in 100 ml pyridine. After two hours the mixture is suspended in water and the solid is filtrated, washed with ethanol and dried in vacuum. The yield is 37 g of 1-p-toluenesulphonyl-4-methylthiosemicarbazide. Said carbazide is refluxed with 19 g of 2-chlorocyclohexanone in 80 ml of ethanol for 3 hours. The precipitate is filtered and dried in vacuum. The yield is 11 g of the product having the structural formula shown in Figure 4B.

<u>B. Preparation of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole (structural formula: Figure 3B)</u>

A quantity of 2 g of the substance prepared in accordance with A (Figure 4B) is suspended in 10 ml of water. After the addition of 10 ml of 48% fluoroboric acid and cooling with ice, 10 ml of 70% nitric acid is added drop-wise. After stirring for 1 hour, the red precipitate is filtered, washed with water and dried in vacuum. The yield is 1.5 g of the fluoroborate salt of the compound shown in fig. 4B. A quantity of 1 g of said salt and 0.42 g of sodium-p-toluenesulphinate are stirred in 30 ml of acetonitrile for 12 hours. The resulting white precipitate is collected and dried in vacuum. The yield is 1 g of the product having the structural formula shown in Figure 3B.

<u>C. Preparation of mono-tosylhydrazone of 3-methylbenzothiazole (structural formula: Figure 4A)</u>

A quantity of 19 g of 3-methyl-benzothiazolone-(2)-hydrazone-hydrochloride-hydrate is suspended in 150 ml of N-methylpyrrolidone together with 1 equivalent of p-toluenesulphonylchloride and 1 equivalent of ZnO. After stirring for 6 hours at 90°C, the mixture is poured in water and the white precipitate is filtered-off. The material is purified by dissolving it in alcoholic NaOH and causing it to precipitate with hydrochloric acid. The yield is 12 g.

<u>D. Preparation of bis-tosylhydrazone of 3-methylb nzothiazole (structural formula: Figure 3A)</u>

This compound was prepared in analogous manner as bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole described under B.

<u>Irradiation experiment.</u>

A quantity of 0,7 wt.% of mono-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole as the precursor (structural formula: Figure 4B), 4 equivalents of 2-phenylindole as the coupler (structural formula: Figure 2 (X), wherein R_3 = phenyl and R_4 = H) and 4 equivalents of benzophenone are suspended in a solution of 15 wt. % of polymethyl methacrylate in cyclohexanone. The mixture obtained is spin coated onto a substrate of ABS (acrylonitrile butadiene styrene). After drying, a layer having a thickness of 50 μm is obtained. After irradiation with an excimer laser (wavelength 308 nm) a violet image is obtained in the exposed parts of the layer. The reaction equation is shown in Figure 5, in which formula XX represents the structural formula of the violet azo-dye formed.

<u>Exemplary embodiment 2.</u>

A quantity of 4 wt.% of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole as the precursor (structural formula: Figure 3B) and 1 equivalent of 2-phenylindole as the coupler are suspended in a two-component polyurethane lacquer. The mixture obtained is spin coated onto a substrate of ABS and dried at 80°C. After drying, a layer having a thickness of 50 μm is obtained. After irradiation with a CO_2 laser (wavelength 10.6 μm; power 4 W/cm^2) a violet image is obtained in the exposed parts of the layer. The reaction equation is shown in Figure 6, in which formula XX represents the structural formula of the violet azo-dye formed.

<u>Exemplary embodiment 3.</u>

A quantity of 4 wt.% of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole as the precursor (structural formula: Figure 3B) and 1 equivalent of 3-methyl-1-phenyl-2-pyrazoline-5-one as the coupler (structural formula: Figure 2 (XI), wherein R_5 = methyl and R_6 = phenyl) are suspended in a two-component polyurethane lacquer. The mixture obtained is spin coated onto a substrate of ABS and dried at 80°C. After drying, a layer having a thickness of 50 μm is obtained. After irradiation with a CO_2 laser (wavelength 10.6 μm; power 4 W/cm^2) a clear orange image is obtained in the exposed areas of the layer. The reaction equation is

shown in Figure 7, in which formula XXX represents the structural formula of the orange azo-dye formed.

Exemplary embodiment 4.

A quantity of 4 wt.% of bis-tosylhydrazone of 3-methylbenzothiazole as the precursor (structural formula: Figure 3A) and 1 equivalent of 1-phenylindole as the coupler are suspended in a two-component polyurethane lacquer. The mixture obtained is spin coated onto a substrate of ABS and dried at 80°C. After drying, a layer having a thickness of 50 μm is obtained. After irradiation with a CO_2 laser (wavelength 10.6 μm; power 4 W/cm^2) a red image is obtained in the exposed areas of the layer. The reaction equation is shown in Figure 8, in which formula XL represents the structural formula of the red azo-dye formed.

Exemplary embodiment 5.

A quantity of 4 wt.% of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole as the precursor (structural formula: Figure 3B) and 1 equivalent of malonitrile as the coupler (structural formula: XIII in Figure 2) are suspended in a two-component polyurethane lacquer. The mixture obtained is spin coated onto a substrate of ABS and dried at 80°C. After drying, a layer having a thickness of 50 μm is obtained. After irradiation with a CO_2-laser (wavelength 10.6 μm; power 4 W/cm^2) a yellow image is obtained in the exposed areas of the layer. The reaction equation is shown in Figure 9, in which formula L represents the structural formula of the yellow azo-dye formed.

Exemplary embodiment 6.

A quantity of 4 wt.% of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole as the precursor (structural formula: Figure 3B) and 1 equivalent of 3-diethylaminoacetoanilide as the coupler are suspended in a two-component polyurethane lacquer. The mixture obtained is spin coated onto a substrate of ABS and dried at 80°C. After drying, a layer having a thickness of 50 μm is obtained. After irradiation with a CO_2 laser (wavelength 10.6 μm; power 4 W/cm^2) a blue image is obtained in the exposed areas of the layer.

The method in accordance with the invention enables azo-dyes of any colour to be formed in a simple manner by means of an IR-laser or UV-laser. An object is coated with a mixture of a precursor and a coupler in a binder, after which decorations and characters can be formed by irradiation with IR-laser light or UV-laser light.

Exemplary embodiment 7.

A quantity of 0.7 wt.% of bis-tosylhydrazone of 4,5-tetramethylene-3-methylthiazole as the precursor (structural formula: Figure 3B), 4-equivalents of 2-phenylindole as the coupler (structural formula: Figure 2 (X), where R_3 = phenyl and R_4 = H) and 4 equivalents of p-nitrobenzoic acid are suspended in a solution of 15 wt.% polymethyl methacrylate in cyclohexanone. The mixture obtained is spin coated onto a substrat of ABS (acrylonitrile butadiene styrene). After drying, a layer having a thickness of 50 μm is obtained. After irradiation with a Co_2-laser (wavelength 10.6 μm) a violet image is obtained in the exposed areas of the layer. The reaction equation is shown in Figure 6, in which formula XX represents the structural formula of the violet azo-dye formed. Dye to the acid medium of the layer, the colour strength is higher than it would be in the absence of p-nitrobenzoic acid.

Exemplary embodiment 8.

A quantity of 0.7 wt.% of tosyl-octylsulphonyl hydrazone of 4,5-tetramethylene-3-methylthiazole as the precursor (structural formula: Figure 10 (LX), 4 equivalents of 2-phenylindole as the coupler (structural formula: Figure 2 (X), wherein R_3 = phenyl and R_4 = H) and 4 equivalents of p-nitrobenzoic acid are suspended in a solution of 15 wt.% polymethyl methacrylate in cyclohexanone. The mixture obtained is spin coated onto a substrate of ABS (acrylonitrile butadiene styrene). After drying, a layer having a thickness of 50 μm is obtained. After irradiation with a Co_2-laser (wavelength 10.6 μm) a violet image is obtained in the exposed areas of the layer. The reaction equation is shown in Figure 10, in which formula XX represents the structural formula of the violet azo-dye formed. By virtue of the presence of the octyl group, the solubility of the precursor in the binder used is enhanced, resulting in a layer which is completely transparent after it has dried. The substitution of an aryl group for the octyl group, as in exemplary embodiment 7, generally results in a more turbid, scattering layer.

Claims

1. A method of marking a surface of an object by means of a laser light beam, said surface being coated with a layer of a mixture which comprises at least a dye precursor, an organic coupler compound having an active hydrogen atom, and a binder, after which the layer is irradiated in accordance with the desired marking by the laser light beam, so that the precursor is converted to a dye in the irradiated areas of the layer, characterized in that an azo-dye is formed as the dye, and that

   - either infrared laser light is used, and that a heterocyclic bis-sulphonylhydrazone is used as the precursor; or
   - ultraviolet laser light is used, and that a heterocyclic mono- or bis-sulphonylhydrazone is used as the precursor, and that a UV-sensitizer is

added in the mixture.

2. A method as claimed in Claim 1, characterized in that the bis-sulphonylhydrazone used is bis-tosylhydrazone of 3-methylbenzothiazole or of 4,5-tetramethylene-3-methylthiazole.

3. A method as claimed in Claim 1, characterized in that the bis-sulphonylhydrazone used is a tosyloctylsulphonyl hydrazone.

4. A method as claimed in Claim 1, characterized in that the UV-sensitizer is benzophenone, 4,4'-dichlorobenzophenone or 4,4'-difluorobenzophenone.

5. A method as claimed in Claim 1, characterized in that mono-tosylhydrazone of 3-methylbenzothiazole or of 4,5-tetramethylene-3-methylthiazole is used as the mono-sulphonylhydrazone.

6. A method as claimed in any one of the preceding Claims, characterized in that a polymer is used as the binder.

7. A method as claimed in any one of the preceding Claims, characterized in that an indole, aniline, phenol or an active methylene compound is used as the organic coupler.

8. A method as claimed in any one of the preceding Claims, characterized in that the object used is made of synthetic resin.

Patentansprüche

1. Verfahren zum Beschriften einer Oberfläche eines Gegenstandes mittels eines Laserlichstrahls, wobei diese Oberfläche mit einer Schicht bedeckt wird aus einem Gemisch, das wenigstens einen Farbzwischenstoff, eine organische Koppelverbindung mit einem aktiven Wasserstoffatom und ein Bildemittel aufweist, wonach die Schicht entsprechend der gewänschten beschriftung mit Hilfe des Laserlichtstrahls belichtet wird, so daß der Zwischenstoff in den belichteten Gebieten der Schicht in einen Farbstoff umgewandelt wird, dadurch gekennzeichnet, daß als Farbstoff ein Azo-Farbstoff gebildet wird, und daß

   - entweder IR-Laserlicht verwendet wird, und daß ein heterozyklisches Bis-Sulphonylhydrazon als Zwischenstoff verwendet wird,
   - oder UV-Laserlicht verwendet wird, und daß ein heterozyklisches Mono- oder Bis-Sulphonylhydrazon als Zwischenstoff verwendet wird, und daß dem Gemisch ein UV-Senisibilisator hinzugefügt wird.

2. Verfahren nach Anspruch 1, dadurch g kennzeichnet, daß das verwendete Bis-Sulphonylhydrazon das Bis-Sulphonylhydrazon von 3-Methylbenzothiazol oder von 4,5-Tetramethylen-3-Methylthiazol ist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das verwendete Bis-Sulphonylhydrazon ein Tosyl-Oktylsulphonyl ist.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der UV-Sensibilisator Benzophenon, 4,4'-Dichlorbenzophenon oder 4,4'-Difluorbenzophenon ist.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Mono-Tosylhydrazon von 3-Methylbenzothiazol oder von 4,5-Tetramethylen-3-Methylthiazol als Mono-Sulphonylhydrazon verwendet wird.

6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß ein Polymer als Bindemittel verwendet wird.

7. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß ein Indol, Anilin, Phenol oder eine aktive Methylenverbindung als organischer Koppler verwendet wird.

8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß der verwendete Gegenstand aus einem Kunstharz hergestellt ist.

Revendications

1. Procédé pour marquer une surface d'un objet au moyen d'un faisceau de lumière laser, ladite surface étant revêtue d'une couche constituée d'un mélange qui comporte au moins un précurseur de teinture, un composé de coupleur organique présentant un atome d'hydrogène actif, et un liant, après quoi la couche est irradiée en conformité avec le marquage souhairé par le faisceau de lumière laser, de sorte que le précurseur est converti en une teinture dans les zones irradiées de la couche, caractérisé en ce qu'une teinture azoïque est formée comme teinture, et en ce que l'on utilise

   - soit de la lumière laser infrarouge, et en ce que l'on utilise une bissulfonylhydrazone hétérocyclique comme précurseur: soit
   - en ce que l'on utilise de la lumière laser ultraviolette, et en ce que l'on utilise une mono ou bissulfonylhydrazone hétérocyclique comme précurseur, et en ce que l'on ajoute un sensibilisateur UV au mélange.

2. Procédé selon la revendication 1, caractérisé en ce que la bissulfonylhydrazone utilisée est de la bistosylhydrazone de 3-méthylbenzothiazole ou de 4,5-tétraméthylène-3-méthylthiazole.

3. Procédé selon la revendication 1, caractérisé en ce que la bissulfonylhydrazone utilisée est une tosyloctylsulfonylhydrazone.

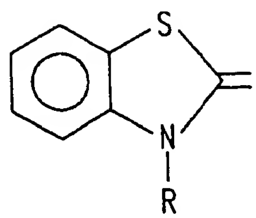
4. Procédé selon la revendication 1, caractérisé en ce que le sensibilisateur UV est de la benzophénone, de la 4,4'-dichlorobenzophénone ou de la 4,4'-difluorobenzophénone.

5. Procédé selon la revendication 1, caractérisé en ce que de la monotosylhydrazone de 3-méthylbenzothiazole ou de 4,5-tétraméthylène-3-méthylthiazole est utilisée comme monosulfonylhydrazone.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce qu'un polymère est utilisé comme liant.

7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce qu'un indole, une aniline, un phénol ou un composé de méthylène actif est utilisé comme coupleur organique.

8. Procédé selon l'une quelconque des revendications précédentes. caractérisé en ce que l'objet utilisé est fabriqué à partir de résine synthétique.



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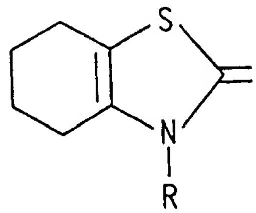
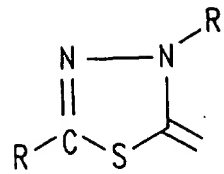
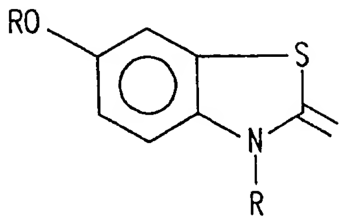


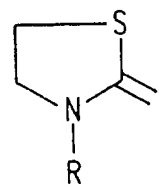
(II)



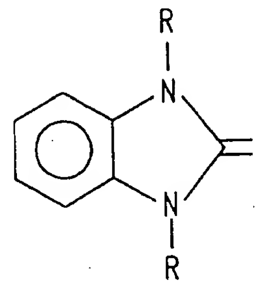
(III)



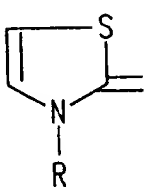
(IV)



(V)

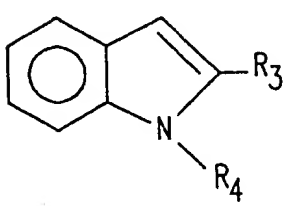


(VI)

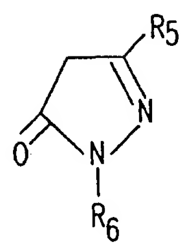


(VII)

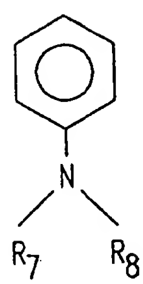
FIG. 1



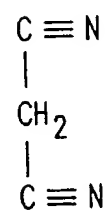
(X)



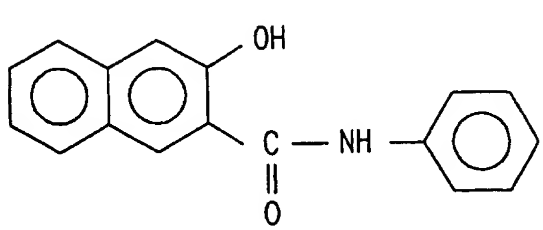
(XI)



(XII)



(XIII)



(XIV)

FIG.2

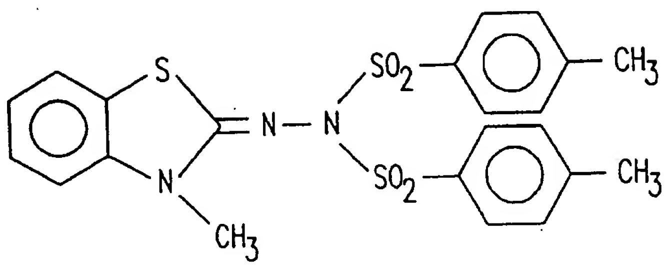


FIG.3A

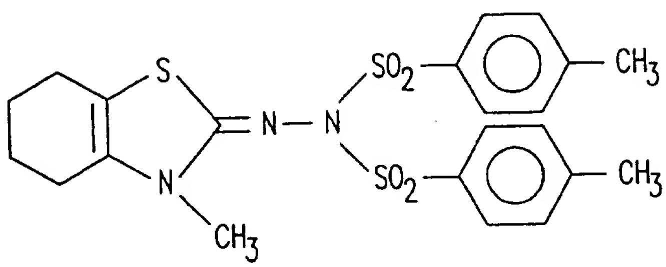


FIG.3B

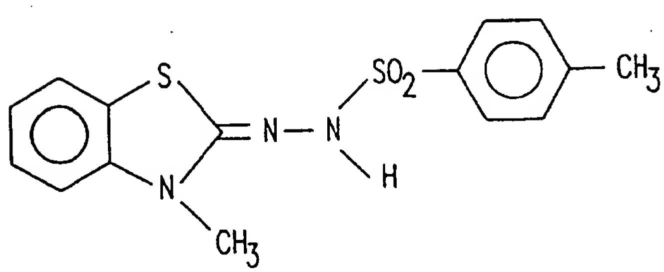


FIG.4A

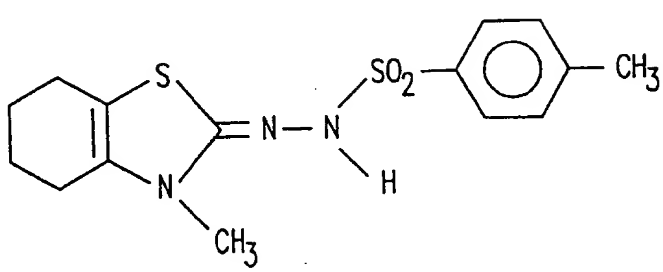
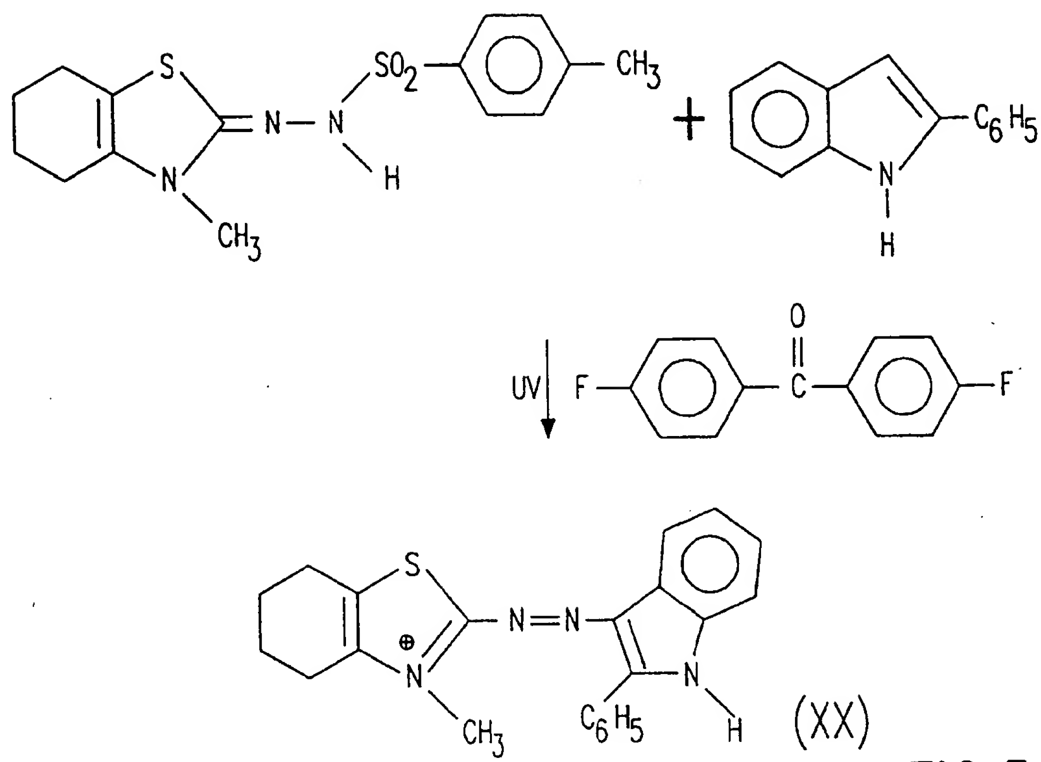
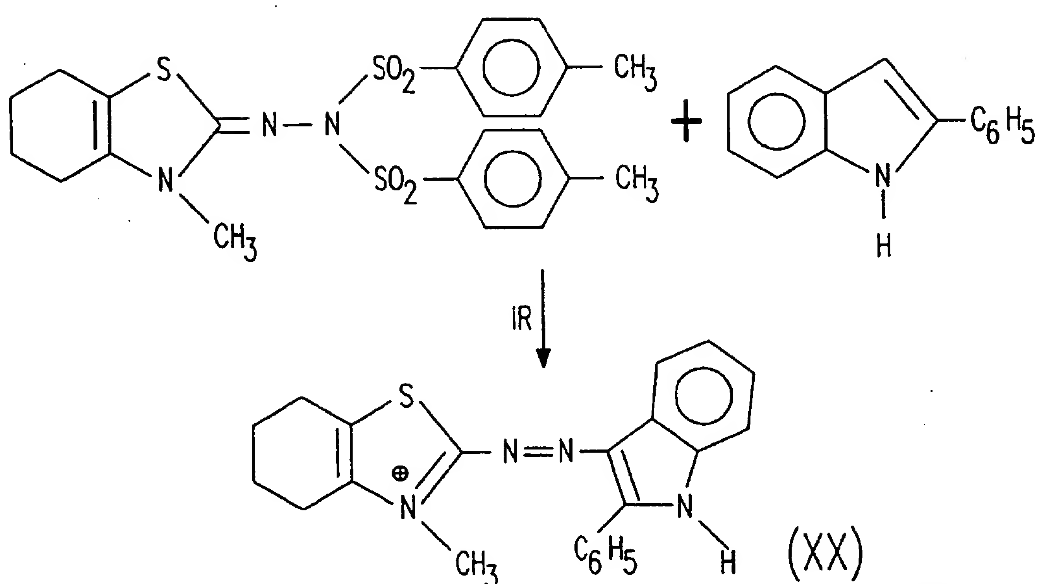


FIG.4B



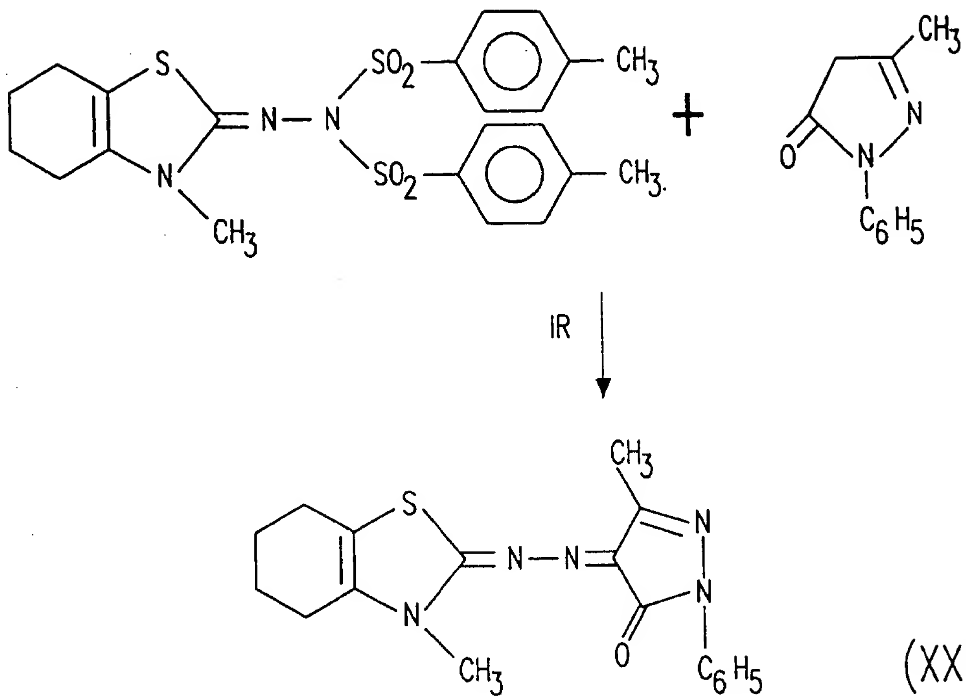
(XX)

FIG.5



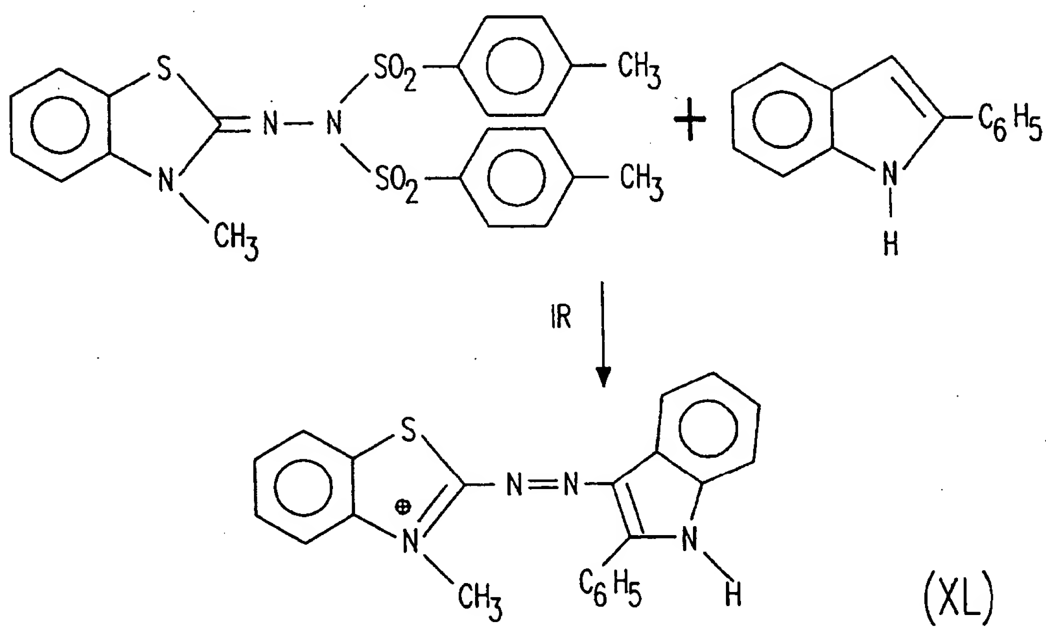
(XX)

FIG.6



(XXX)

FIG.7



(XL)

FIG.8

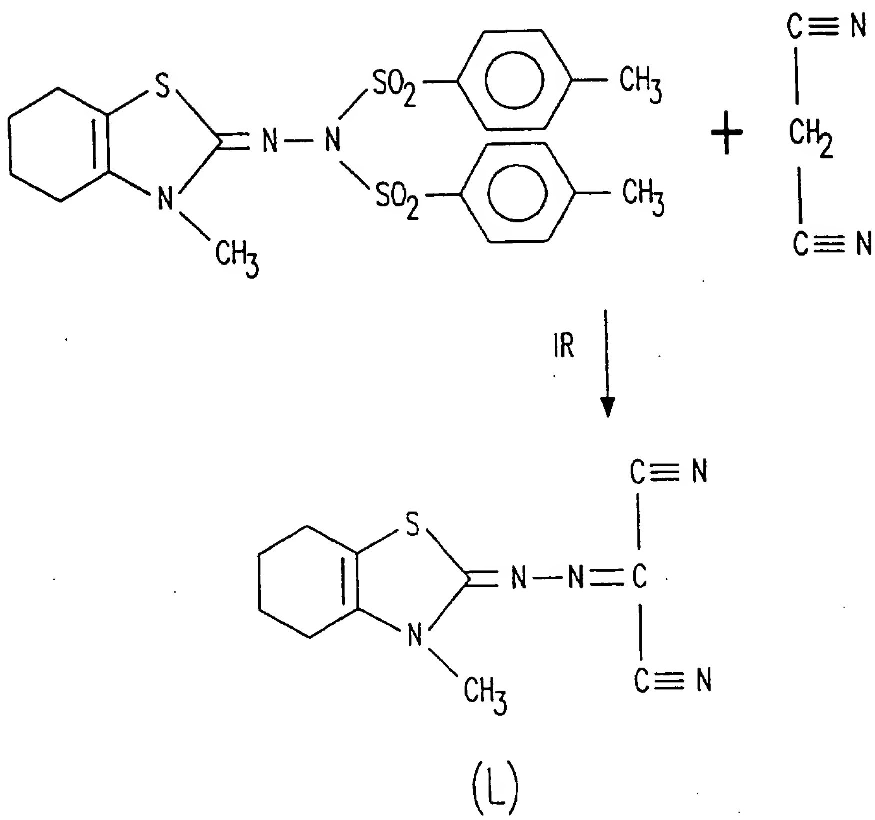

S
N
CH_3
N — N
SO_2
SO_2
CH_3
CH_3
+
C≡N
CH_2
C≡N
IR
N—N=C
(L)

FIG.9

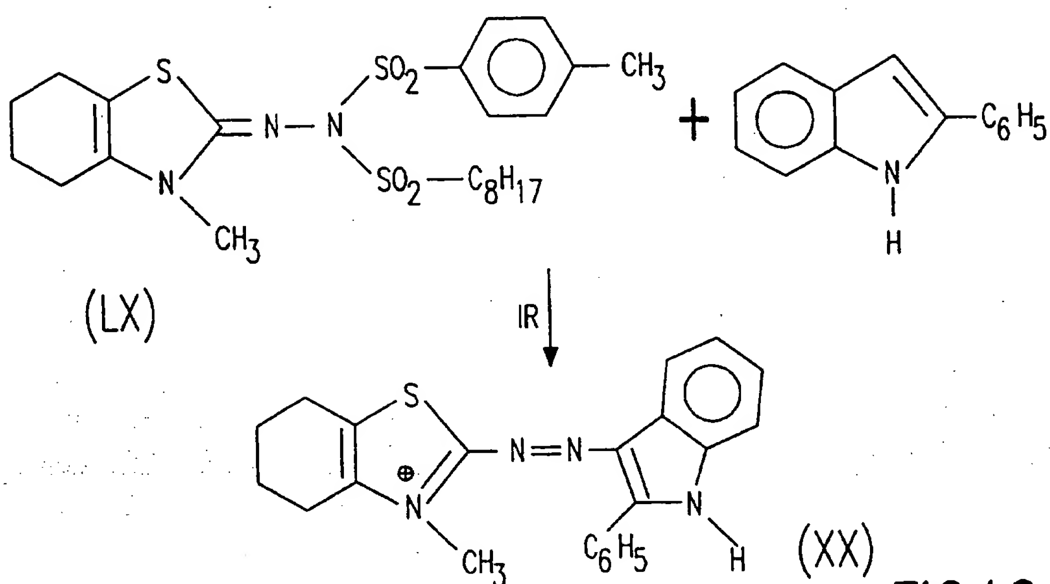

S
N
CH_3
N — N
SO_2
CH_3
SO_2 — C_8H_{17}
(LX)
+
C_6H_5
N
H
IR
N=N
⊕
C_6H_5
(XX)

FIG.10